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Study on the separation performance of the multi-channel reduced graphene oxide membranes

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ABSTRACT

The multi-channel reduced graphene oxide membranes with separation function have been synthesized by a simple hydrothermal reduction method and vacuum filtration. In the as-synthesized membranes, the size, number, and type of the nanochannels can be controlled by the reduced temperature. The flux and retention rate of solution are investigated by filtering different size dye molecules. The interception and adsorption effect in the separation process are discussed. Furthermore, the sizes of the nanochannels in the membranes prepared by the different reduced temperatures are estimated. The results indicate that the multi-channel reduced graphene oxide membranes have potential application in water purification area.

1. Introduction

Graphene is an excellent monoatomic two-dimension material, which possesses excellent physical and chemical properties, such as great mechanical strength, flexibility, high specific surface area, and chemical inertia [1–4]. Theoretical studies have demonstrated that the graphene membrane with nanochannel has superior separation performance for water and gas [5,6]. However, there are still many obstacles in manufacturing the large-scale membranes [7]. Graphene oxide (GO) is a functionalized graphene derivative. Recently, laminated GO membrane attracts tremendous attention for its application in separation and purification technology [8–10]. The GO membranes have compact structure and the as-formed nanochannels in the membranes are very narrow, which influences their permeation performance. It is an important step for separation application to control the size of the nanochannels in the GO membranes. Recently, researchers have designed some special nanochannels in the two-dimensional GO membranes through several approaches including chemical and physical methods to achieve the ideal separation effect. In addition, some materials can be inserted into the GO membranes to expand the layer spacing between the sheets or add the mesoporous. For example, Peng et al. successfully prepared a mesoporous GO membrane by introducing in-plane mesopores of GO by re-oxidation with strong oxidizing agent such as $KMnO_4$. The nanopores not only increase new path for water molecules, but also decrease the distance of water passing through the membrane. These membranes exhibited an excellent separation performance with 88.5% rejection for Evans-blue molecules and water permeability of 191 $Lm^{-2}\,h^{-1}\,bar^{-1}$ [11]. Xu et al. prepared graphene oxide-TiO_2 composite films by inserting inter-sheet TiO_2 particles and used the films as filtration membranes to remove effectively methyl orange and rhodamine B from water [12].

Reduced graphene oxide (rGO) is also a two dimensional material with graphene domains, defects, and residual oxygen-containing groups on the surface of the sheet [13]. The laminar rGO membrane has been considered as a promising candidate in separation membranes, because rGO can form highly ordered membranes with two-dimension nanochannels between two rGO sheets. Especially, water can permeate fast through the nanochannels between pristine graphene regions due to the hydrophobic graphene wall with ultralow friction [14]. Additionally, the residual functional groups on the surface of the rGO sheets such as hydroxyl, carboxyl, and alkoxy, can bring hydrophilicity, which is also beneficial to enhance the percolation of water. Han et al. fabricated ultrathin and robust rGO nanofiltration membranes from dilute base-refluxing reduced GO by vacuum assisted assembly strategy. The dilute rGO sheets stacked with each other forming sub-1-nm sized 2D nanocapillaries. Accompanied by the relative high pure water flux (21.8 $Lm^{-2}\,h^{-1}\,bar^{-1}$), the resulting ultrathin graphene

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nanofiltration membranes showed high retention rates for organic dyes and moderate retention rates for salts [15]. Sun et al. prepared GO/titania membrane by intercalating monolayer titania (TO) nanosheets into GO laminates. The sizes of nanochannels in the GO/TO hybrid membranes were adjusted by intercalating monolayer titania nanosheets. And the GO/TO hybrid membranes were reduced by mild ultraviolet reduction. The rGO/TO membranes exhibited excellent water desalination performances [16]. In summary, it will be very important for the separation membrane application to control the size of the nanochannels in the rGO membrane.

In this paper, multi-channel rGO membranes are synthesized using the simple hydrothermal reduction method. The sizes of the nanochannels are successfully adjusted by hydrothermal reduction temperature. The nanochannels are attributed to the inter-sheet two-dimention nanochannels and in-plane nanopores by analyzing the change of the morphologies, chemical functional groups, and defects of rGO membranes. The potential uses are studied in water purification. Furthermore, the interception and adsorption of filtered process for the rGO membranes are discussed.

2. Experimental

2.1. Synthesis of GO/rGO

Graphene oxide (GO) sheets were prepared from natural graphite (325 Mesh) according to the method reported by Hummers [17]. Reduced graphene oxide (rGO) was prepared by hydrothermal reduction method, which is simple and environmentally friendly. Firstly, 35 ml of GO solution (1 mg/ml) was placed in the hydrothermal autoclave reactor. Then, the hydrothermal autoclave reactor was put into a drying oven for 2 h at 80 °C. A series of samples were obtained under different reduction temperature of 100 °C, 120 °C, 140 °C, 150 °C, 160 °C and 180 °C, respectively. The as-prepared rGO was marked as rGO_{80}, rGO_{100}, rGO_{120}, rGO_{140}, rGO_{150}, rGO_{160} and rGO_{180}, respectively.

2.2. Preparation of rGO membrane

The rGO separation membranes were fabricated by vacuum filtration. 10 mg as-prepared rGO is dispersed in 40 ml water. The rGO solutions were filtered through the mixed cellulose ester membrane (MCEM, 47 mm in diameter, 0.22 μm pore size). The rGO membranes were uniformly assembled on the surface of the MCEMs. The as-prepared membranes were dried at room temperature overnight. Finally, the rGO separation membranes were achieved. We marked the rGO layered membrane prepared at different hydrothermal reduction temperature as the $rGOM_{temperature}$ ($rGOM_{80}$, $rGOM_{100}$, $rGOM_{120}$, $rGOM_{140}$, $rGOM_{150}$, $rGOM_{160}$ and $rGOM_{180}$).

2.3. Characterization

The morphologies of the GO/rGO films were analyzed by transmission electron microscopy (TEM, JEM-2100). The cross section of the GO/rGO membranes were evaluated by field-emission scanning electron microscope (FESEM, Hitachi S-4800). Fourier transform infrared (FTIR) spectra were conducted through Bruker Optics Tensor 27 instrument. The Raman spectra of GO and rGO were recorded on Raman microscope spectrometer (Thermo Scientific, DXR). The ultraviolet–vis (UV–vis) absorption spectra were carried out by UV-3200.

2.4. Separation performance

By vacuum filtration, the organic dye solution (Methyl blue ($1.4 \times 2.4\,nm^2$) and Rhodamine B ($1.8 \times 1.4\,nm^2$)) have been filtered using the rGOMs [18,19]. The separation properties (flux and retention rate) of rGOMs were investigated. The concentrations of Methyl blue (MB) and Rhodamine B (Rh B) solutions were both 20 μmol/L. The filtrate and residual solution were examined by UV–vis spectrophotometer to confirm the concentration of filtrate and residual solution. The fluxes were measured by recording the volume and time of filtrate to flow through the as-prepared filtered membranes.

3. Results and discussion

As shown in Fig. 1(a)–(f), the morphology of the GO/rGO sheets is characterized by TEM. The GO sheets have a smooth surface and high transparency, as shown in Fig. 1(a). This indicates that GO have been fully exfoliated and well-dispersed in aqueous solutions. When the hydrothermal temperature increases to 80 °C, small amounts of wrinkles are generated on the rGO surface, as displayed in Fig. 1(b). The wrinkled structure represents a curled and corrugated morphology of rGO sheet. Compared with the rGO_{80} sheets, the wrinkles on the surface of rGO_{120} sheets have been increased, as depicted in Fig. 1(c). With the reduction temperature elevating to 140 °C, we can observe a large number of folds on the surface of rGO, as shown in Fig. 1(d). As the hydrothermal reduction temperature is raised to 160 °C, not only increasing number of folds are generated but also a number of pores start to arise from the structural defects on the surface of the rGO sheets, as seen in Fig. 1(e). The wrinkles have random size and the diameters of the nanopores are about tens of nanometers. A number of the overlapped regions of the rGO sheets are formed and the thickness of the rGO sheets has been increased (Fig. 1(e)). This is attributed to the fact that the folded-edge sheets partially overlap and aggregate due to Van der Waals binding between rGO sheets [20]. The higher temperature can also improve the vibration energy of carbon atoms, which promotes the formation and expansion of the nanopores. With the reduction temperature increasing to 180 °C, the size and number of the wrinkles, the overlapped region and nanopores on the surface of rGO sheet have increased, as presented in Fig. 1(f).

The rGO membranes prepared under different hydrothermal reduction temperature are assembled on the MCEM by vacuum filtration. The cross sections of the rGO membranes are characterized by FESEM, as shown in Fig. 2(a)–(c). All membranes have layered structure. For the $rGOM_{100}$, the fracture profile displays a uniform layered structure, as seen in Fig. 2(a). As the hydrothermal temperature arises to 140 °C, the stacking membranes exhibit increasing inter-layer spacing, as depicted in Fig. 2(b). Unlike the $rGOM_{100}$ and $rGOM_{140}$ membranes, the loose and disorderly layered structure are observed from the fracture edge of the $rGOM_{160}$, as shown in Fig. 2(c).

To investigate the evolution of randomly distributed functional groups located both at edges and on the basal plane with increasing of the hydrothermal reduction temperature, infrared (IR) absorption spectroscopy is carried out. The infrared spectra of GO and rGO for different hydrothermal reduction temperature (80–180 °C) are presented in Fig. 3(a). There are two main frequency regions at 1000–2000 cm^{-1} and 2500–3700 cm^{-1} which are related to the main functional groups on both the edges and the basal plane of GO and rGO, such as alkoxy, epoxy, hydroxyl, carboxyl and adsorbed water [21]. The two regions are marked as the red and gray shadow, respectively. The random distribution of functional groups can complicate the analysis of the infrared spectra because there is a range of environments for each species, leading to fre-